

HYDROGEN SEPARATION MEMBRANES FOR VISION 21 ENERGY PLANTS

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ABSTRACT

This report summarizes work performed at Eltron developing dense composite materials for hydrogen separation membranes. An overview of the hydrogen permeation characteristics of multi-phase ceramic and ceramic/metal membranes is provided.

INTRODUCTION

Eltron Research and team members CoorsTek, Süd Chemie, and Argonne National Laboratory are developing dense composite membranes for separating hydrogen from gas mixtures produced during industrial processes, such as coal gasification. This project was motivated by the National Energy Technology Laboratory (NETL) Vision 21 initiative, which seeks to economically minimize the environmental impact associated with the use of fossil fuels. This developing technology addresses the DOE Vision 21 initiative in two ways. First, dense composite membranes potentially offer a simple and inexpensive solution for pure hydrogen separation, which can be easily incorporated into Vision 21 energy plants. Second, this process could contribute to a reduction in the cost of hydrogen, which is a clean burning fuel under increasing demand as supporting technologies are developed for hydrogen utilization and storage.

Currently, this project is focusing on three basic categories of membranes: i) ceramic/ceramic composites, ii) high-temperature ceramic/metal composites (cermets), and iii) intermediate-temperature composites. A comparison of these membranes is presented in Table 1. The ceramic/ceramic composites demonstrate the lowest hydrogen permeation rates, with a maximum of approximately $0.1 \text{ mL min}^{-1} \text{ cm}^{-2}$ for 0.5-mm thick membranes at 800 to 950°C. Under similar conditions, cermets achieve a hydrogen permeation rate near $1 \text{ mL min}^{-1} \text{ cm}^{-2}$, and the metal phase also improves structural stability and surface catalysis for hydrogen dissociation. Furthermore, if metals with high hydrogen permeability are used in cermets, permeation rates near $4 \text{ mL min}^{-1} \text{ cm}^{-2}$ are achievable with relatively thick membranes. Intermediate-temperature cermets are more difficult to fabricate and the characteristics of these materials have not yet been thoroughly determined. However, experimental results at this time indicate that roughly an order of magnitude improvement in hydrogen permeation relative to high-temperature analogs at temperatures near 400°C is possible. Consequently, the operating temperature of these membranes will be more compatible with upstream gas cleanup systems.

Table 1. Summary of Hydrogen Separation Membrane Characteristics.

Composite Membrane	Thickness (mm)	Operation Temperature (°C)	Approx. Max. Separation Rate (mL min⁻¹ cm⁻²)	Ambipolar Conductivity (S/cm)	Permeability (mol m m⁻²s⁻¹ Pa^{-0.5})	Potential Advantages	Potential Disadvantages
Ceramic/Ceramic	0.1 to 0.5	700 to 950	0.1	1×10^{-4} to 5×10^{-3}	N/A	<ul style="list-style-type: none">• Inexpensive• Resistant to poisons	<ul style="list-style-type: none">• Low H₂ flux• Brittle
High-Temperature Cermet	0.1 to 0.5	700 to 950	1.0	2×10^{-4} to 1×10^{-2}	N/A	<ul style="list-style-type: none">• Better H₂ flux than pure ceramics• Inexpensive• Integrated catalyst• Less brittle	<ul style="list-style-type: none">• Susceptible to poisons• Lower H₂ flux than H₂-perm. metal
High-Temperature Cermet w/ H ₂ -perm metal	0.1 to 0.5	550 to 950	4	N/A	$\approx 10^{-8}$ 600 to 950°C	<ul style="list-style-type: none">• High H₂ flux• Integrated catalyst• Less brittle	<ul style="list-style-type: none">• Expensive• Susceptible to poisons
Intermed.-Temp. Composite Membrane	0.05 to 0.5	300 to 750	>10	N/A	$\approx 10^{-7}$ 380 to 450°C	<ul style="list-style-type: none">• Highest H₂ flux• Compatible with desulfurization system	<ul style="list-style-type: none">• Susceptible to poisons• Difficult to fabricate

SUMMARY OF PROJECT RESULTS

Measurements and Calculations

Membrane samples were sealed on opposite sides to alumina feed and sweep tubes using a variety of materials, such as Pyrex rings for high-temperatures or copper gaskets for intermediate temperatures. Hydrogen transport measurements were obtained over the temperature range from 350° to 950°C, depending on the type of membrane being tested. Inlet hydrogen was diluted with helium, which also enabled evaluation of the quality of the membrane seal to the alumina feed and sweep tubes. Concentrations of hydrogen and helium in the inlet and sweep streams were determined by gas chromatographic (GC) analysis with thermal conductivity detection. Ultra-high purity argon was used as the sweep gas and GC carrier gas to optimize detection limits for hydrogen and helium. Concentrations of hydrogen and helium were calculated from plots of chromatographic peak area versus concentration for a set of standards.

Permeation rates for hydrogen, J ($\text{mL min}^{-1} \text{ cm}^{-2}$), were calculated according to,

$$J = \left[C_{H_2,out} - C_{He,out} \left(\frac{C_{H_2,in}}{C_{He,in}} \right) \right] F_T \frac{1}{A} \quad (1)$$

where $C_{H_2,out}$, $C_{He,out}$, $C_{H_2,in}$, and $C_{He,in}$ are the concentrations (vol. fraction) of hydrogen and helium in the outlet sweep stream and inlet feedstream, respectively, F_T is the total flow rate (mL/min) on the sweep side, and A is the membrane area (cm^2). This equation corrects the hydrogen permeation rate for leaks by subtracting the permeate helium (adjusted for the relative inlet concentrations of hydrogen and helium). In this equation, it is assumed that hydrogen and helium leak at the same rate, which was not necessarily true for the small leaks typical in these types of experiments. Accordingly, only data obtained with leak rates less than a few percent of the total hydrogen permeation rate were retained.

In the absence of hydrogen permeable metals, hydrogen transport through dense high-temperature ceramic membranes is limited by mixed proton and electron conduction, which is referred to as ambipolar conductivity, σ_{amb} (S/cm). From the measured J and membrane thickness, t (cm), the apparent σ_{amb} was calculated from,

$$\sigma_{amb} = \frac{JnFt}{E} \quad (2)$$

where n is the number of moles of charge carrier per mole of hydrogen, F is Faraday's constant, and E is the Nernst potential across the membrane. The Nernst potential was calculated from,

$$E = -\frac{RT}{nF} \ln \frac{C_{H_2,out}}{C_{H_2,in}} \quad (3)$$

where R is the gas constant and T is temperature. Since σ_{amb} accounts for the membrane thickness and hydrogen concentration gradient, it is a convenient parameter for comparing the performance of membranes tested under different conditions. Membrane proton and electron conductivity, σ_{H^+} and

σ_{e-} , is proportional to σ_{amb} according to the relationship,

$$\frac{1}{\sigma_{amb}} \propto \frac{1}{\sigma_{H^+}} + \frac{1}{\sigma_{e-}} \quad (4)$$

Therefore, for samples with very high electron conductivity, $\sigma_{amb} \sim \sigma_{H^+}$.

The mechanism for hydrogen transport through membranes containing hydrogen permeable metals is different than for ceramics, and membrane permeability P ($\text{mol m m}^{-2} \text{s}^{-1} \text{Pa}^{-n}$) was used rather than σ_{amb} to characterize performance. Permeability was calculated according to,

$$P = \frac{Jt}{p_f^x - p_s^x} \quad (5)$$

where p_f^x and p_s^x are the hydrogen partial pressures on the feed and sweep sides, respectively. It was assumed that the exponent x is 0.5 according to Sieverts' Law; however, significant deviation from the square root dependence can occur when permeation is limited by surface kinetics or mass transport.¹ An important distinction between these two categories of membranes is apparent by comparing Equations 3 and 5. For proton conducting ceramic membranes hydrogen transport is dependent on the ratio of hydrogen concentrations on opposite sides of the membrane; whereas, for membranes with hydrogen permeable metals transport is dependent on the difference in concentrations.

Ceramic/Ceramic Composites

Ceramic/ceramic composites incorporate a proton conducting perovskite phase with an electron conducting ceramic second phase. This combination can be achieved either by excessive doping of a parent perovskite with appropriate transition metal oxides, or by mixing distinct proton and electron conducting ceramic phases. Using the former method, a fraction of the transition metal dopant is introduced into the perovskite lattice during calcination, which generates oxygen vacancies and promotes proton conductivity. The remainder of the transition metal typically results in a metal oxide with high electron conductivity. Alternatively, the latter method requires mechanical mixing of ceramics with optimal proton and electron conduction, and the challenge is to achieve a dense membrane without migration of cations between the two phases during sintering.

Figure 1 shows typical results for ceramic/ceramic composite membranes prepared by overdoping a precursor perovskite with a transition metal oxide. Both samples were composed of the same perovskite and metal oxide phases; however, sample A contained three times the amount of transition metal as sample B. As evident in the figure, increasing the transition metal content dramatically improved hydrogen permeation (six-fold increase at 950°C). Moreover, sample A was twice as thick as sample B (1.3 mm compared to 0.65 mm), which indicated an overall 12-fold improvement in performance by tripling the transition metal content of the material. These results corresponded to a maximum apparent σ_{amb} of $1.2 \times 10^{-3} \text{ S/cm}$ for sample A and $8.9 \times 10^{-5} \text{ S/cm}$ for sample B. Arrhenius plots of $\ln(\sigma_{amb} T)$ versus $1/T$ indicated an activation energy, E_a , for hydrogen permeation of 75 and 113 kJ/mol for samples A and B, respectively.

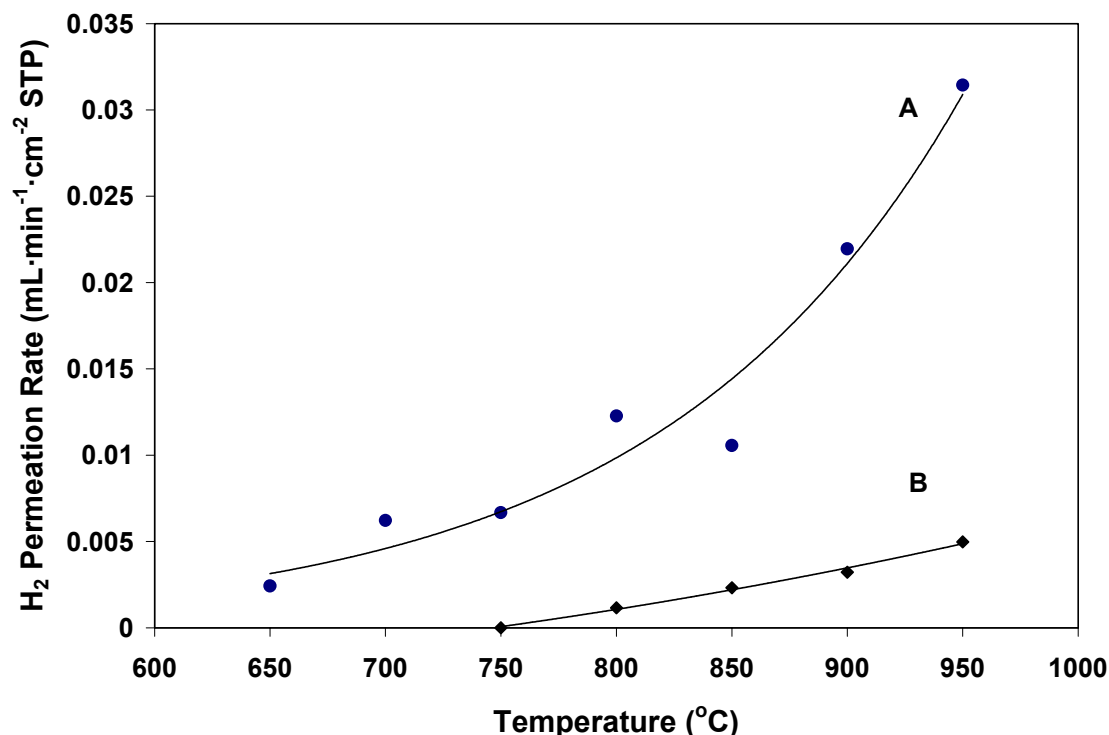


Figure 1. Hydrogen permeation as a function of temperature for typical ceramic/ceramic composite membranes. Sample A was 1.3 mm thick and sample B was 0.65 mm thick. Both samples had a thin catalyst coating on each side of the membrane. The feed gas was 100 mL/min of humidified 80/20 H₂/He. The sweep gas was 100 to 120 mL/min Ar.

X-ray diffraction patterns indicated that roughly the same quantity of transition metal was incorporated into the perovskite phase of each sample. Therefore, proton conductivity was equivalent for both samples and the improved performance of sample A was the result of increasing the percentage of the electron conducting phase. However, increasing the transition metal content beyond the level of sample A resulted in a rapid decrease in performance and loss of the pseudo-cubic proton conducting perovskite phase. It is likely that sample A had an optimum level of electron conductivity so that hydrogen permeation was limited primarily by the sample proton conductivity, and σ_{amb} was at a maximum. Further increasing the electron conducting phase content decreased performance by reducing the percentage of the rate-limiting proton conducting phase.

Although hydrogen permeation through these ceramic/ceramic composites is lower than other candidate membranes, the permeation process is bulk diffusion limited and a significant increase in hydrogen flux could be achieved by minimizing membrane thickness. The nature of these materials makes them suitable for high-temperature applications, and since there are no pure metals in the compositions there is potential for higher tolerance to sulfur and carbon monoxide. Similarly, although some of the best proton conducting perovskites are unstable in carbon dioxide and moisture, simple modifications to the composition and/or operating conditions can dramatically increase stability with minimal reduction in hydrogen permeation. Ultimately, the greatest challenge for these materials likely will be to fabricate supported dense thin films with adequate mechanical strength.

High-Temperature Cermets

An alternative to the ceramic/ceramic composites is to combine a proton-conducting ceramic phase with a metallic phase. The most obvious advantage of this approach is that very high electron conductivity can be achieved with a small quantity of the metal, thereby maximizing the content of the proton conducting phase. Figure 2 shows hydrogen permeation as a function of membrane thickness and temperature for a proton conducting ceramic with a metal phase content of 44 wt.% (≈ 34 vol.%). The maximum hydrogen permeation rate was $0.84 \text{ mL min}^{-1} \text{ cm}^{-2}$ for a 0.16-mm thick membrane at 950°C . This permeation rate was more than 25 times higher than the ceramic/ceramic composites and these cermets demonstrated a maximum σ_{amb} of 0.013 S/cm and an E_a near 20 kJ/mol .

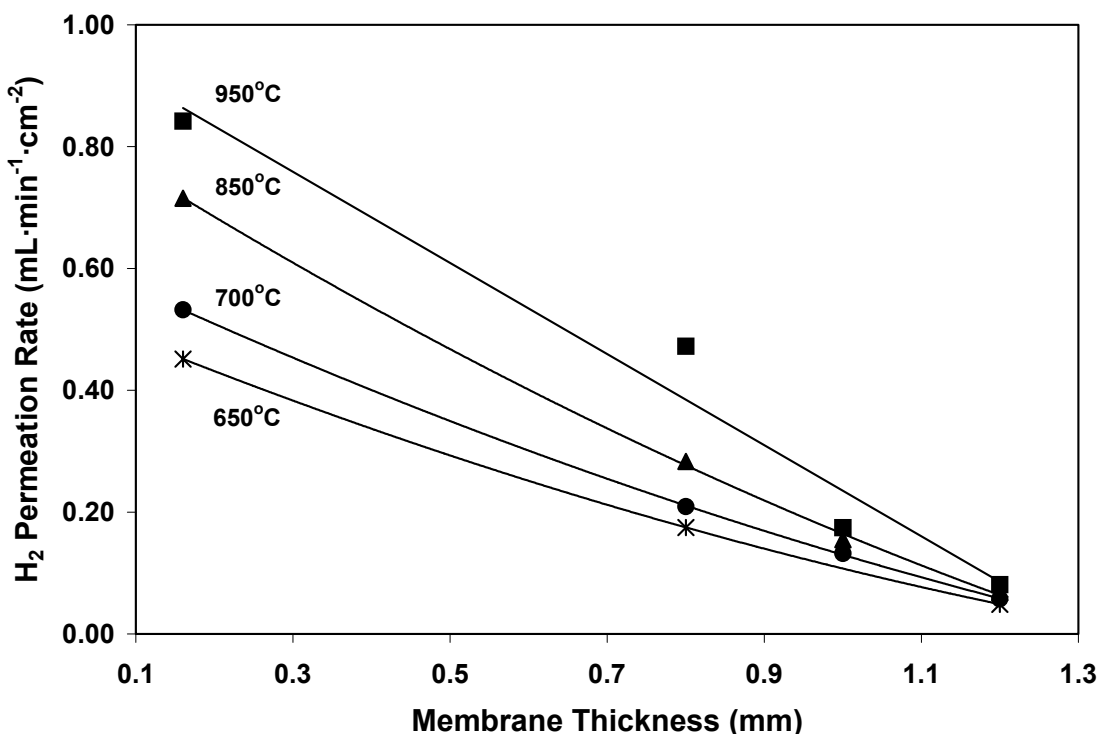


Figure 2. Hydrogen permeation as a function of membrane thickness and temperature for a cermet containing a proton conducting perovskite with 44 wt.% metal phase. The feed gas was 100 mL/min of humidified 80/20 H_2/He . The sweep gas was 100 to 120 mL/min Ar.

The optimum metal content of ≈ 44 wt.% was determined from hydrogen permeation tests for a series of cermets ranging from approximately 30 to 50 wt.% metal phase. Each of these samples demonstrated roughly the same high level of electronic continuity when tested with an ohmmeter (0.1 to 0.3Ω), so it was assumed that the sample with the lowest metal content (*i.e.*, the highest proton conducting phase content) would generate the highest hydrogen flux. Instead, hydrogen permeation increased steadily between about 30 and 44 wt.% metal, then rapidly decreased with increasing metal content. Rather than a dependence on electron conductivity for these samples, it is likely that the higher percentage of metal phase resulted in improved hydrogen exchange catalysis at

the membrane surface, as also was observed by Siriwardane *et al.* for similar materials.² Specifically, as the bulk metal concentration increased, the membrane surface roughness increased due to formation metal nodules that facilitate dissociative adsorption of hydrogen on the feed side, and desorption of hydrogen on the permeate side. However, beyond the optimum value, the rapid decrease in permeation probably was due to decreased continuity of the proton conducting phase.

The metal phase of the above cermet had some hydrogen permeability, but the contribution was insignificant and the metal phase acted only as an electron conductor and catalyst. In contrast, a dramatic increase in hydrogen transport was achieved by incorporating metals and alloys with high hydrogen permeability. Figure 3 shows hydrogen permeation as a function of temperature and membrane thickness for cermet using the same ceramic phase as above and 57 wt.% (40 vol.%) of a hydrogen permeable metal. Hydrogen permeation at 950°C increased from 0.47 to 3.9 mL min⁻¹ cm⁻² as the membrane thickness was reduced from 1.1 to 0.23 mm. This maximum permeation rate corresponded to a hydrogen permeability of 2.2×10^{-8} mol m m⁻² s⁻¹ Pa^{-0.5}, which was only slightly lower than anticipated for the pure metal. As evident in Figure 3, these materials also demonstrated high permeation at intermediate temperatures, and Arrhenius plots of $\ln(P)$ vs. $1/T$ indicated an apparent E_a less than 15 kJ/mol.

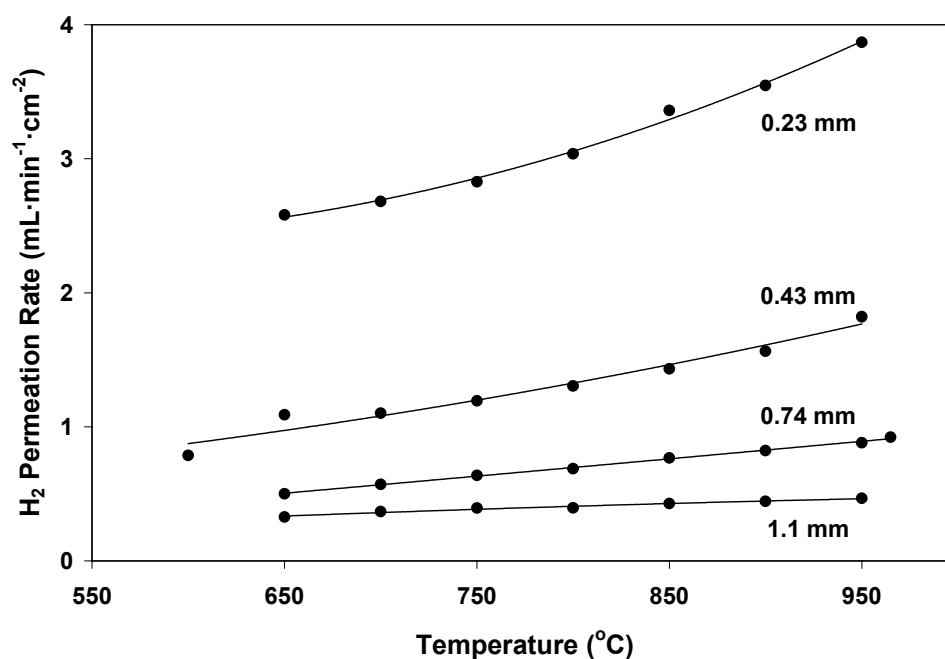


Figure 3. Hydrogen permeation as a function of membrane thickness and temperature for a cermet containing a proton conducting perovskite with 57 wt.% of a hydrogen-permeable metal phase. The feed gas was 100 mL/min of humidified 80/20 H₂/He. The sweep gas was 100 to 120 mL/min Ar.

In addition to higher electron conductivity and improved surface catalysis, these cermet membranes have much higher mechanical strength than the ceramic/ceramic analogs. For example, four-point bend flexural strength measurements on the ceramic phase of the above cermets demonstrate a value near 70 MPa, whereas, the cermets achieve values near 150 MPa. Similar improvements in Weibull Modulus were attained as well. Furthermore, diffusion of constituents between the two phases is less prominent than for ceramic/ceramic composites, so fabrication

generally is much easier. Despite these advantages, to enable commercially viable hydrogen separation rates it still will be necessary to produce supported dense thin cermet films. Moreover, the metal phase will be very susceptible to poisoning by common feedstream constituents, such as sulfur and carbon monoxide. Accordingly, cermet membranes likely will require a higher degree of gas cleanup prior to entering the hydrogen separation unit.

Intermediate-Temperature Composites

More recently, effort has focused on development of composite membranes that utilize inexpensive hydrogen permeable metals and operate at intermediate temperatures that are more compatible with gas cleanup technologies. This approach was initiated by first testing the permeation characteristics of candidate metals without incorporation into cermets. Figure 4 shows hydrogen permeation as a function of temperature for a 0.13-mm thick composite metal membrane. At only 400°C, this membrane permeated nearly 20 mL min⁻¹ cm⁻² of hydrogen and permeation increased steadily to 25 mL min⁻¹ cm⁻² at 470°C. Increasing the sweep rate dramatically increased permeation and at 400°C a maximum permeation rate of 27 mL min⁻¹ cm⁻² was attained using a sweep rate of 568 mL/min. These results corresponded to a maximum diffusivity of 1 x 10⁻⁶ m²/s, a permeability of 2 x 10⁻⁷ mol m m⁻² s⁻¹ Pa^{-0.5}, and an E_a of approximately 21 kJ/mol. Despite these very high permeation results, this type of membrane is not expected to be sufficiently stable for commercial applications. Accordingly, the goal now is to incorporate this economical and highly permeable metal into a cermet.

Unlike expensive hydrogen permeable metals (*e.g.*, Pd and its alloys), fabrication of a cermet based on the above material is difficult due to metal reactivity. Initial attempts to produce cermet analogs resulted in structurally stable membranes; however, in addition to the ceramic and metal phases, undesired oxide and carbide phases also were present. Adjusting the sintering conditions and atmosphere improved the membrane compositions, and most of the residual undesired phases were limited to the membrane surface. Slight sanding of the surfaces nearly eliminated evidence of these phases in X-ray diffraction patterns.

Figure 5 contains preliminary results for a thick (0.83-mm) cermet membrane with 60 vol.% metal phase. The ceramic phase had negligible proton conductivity and the metal phase was the primary component of the composite metal membrane in Figure 4. The membrane did not contain a catalyst to promote hydrogen dissociation or protect the surface. Only results at high-temperature were obtained (750°C) and the data shows a substantial decrease in permeation from 0.37 to 0.21 mL min⁻¹ cm⁻² over 193 minutes of testing. Post-run X-ray diffraction analysis revealed dramatic changes to both the feed and sweep sides of the membrane, which explain the loss of permeation. Specifically, the sweep side demonstrated a reduction in the metal-to-ceramic ratio and a significant quantity of the oxide of the metal phase (likely from an air leak in the system). The feed side also showed a reduction in the metal-to-ceramic ratio, as well as a small quantity of an unidentified phase. SEM analysis of the membrane before and after permeation measurements corroborated the X-ray diffraction results and demonstrated major morphological changes, including an increase in surface roughness and extensive micro-cracks. These results highlight the reactivity of the metal phase and underscore the need for a protective/catalytic surface coating with this category of membrane. Furthermore, it is likely that this test temperature was much too high for this material.

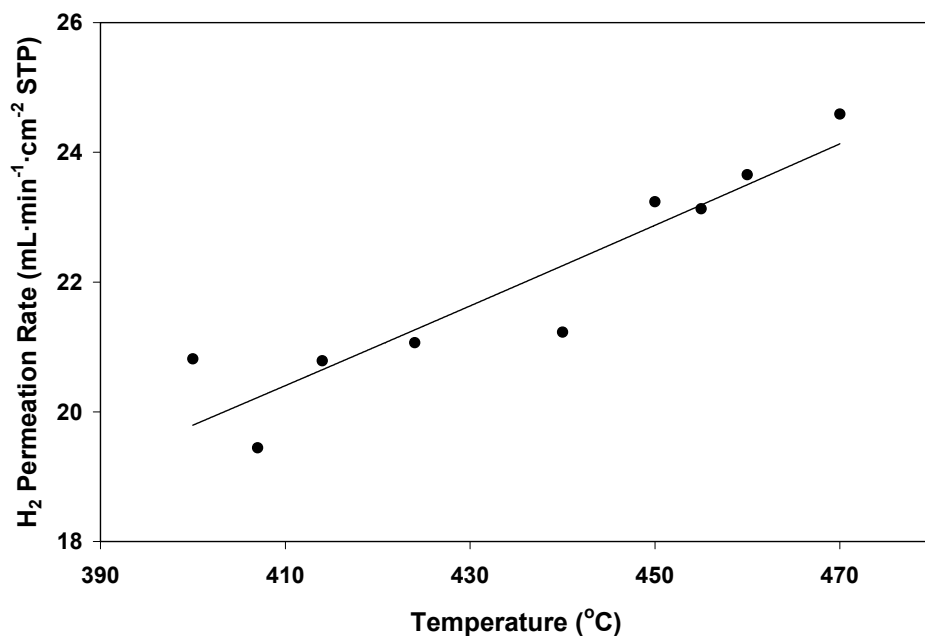


Figure 4. Hydrogen permeation as a function of temperature for a 0.13-mm thick composite metal membrane. The feed gas was 170 mL/min 80/20 H₂/He and the sweep gas was 250 mL/min Ar.

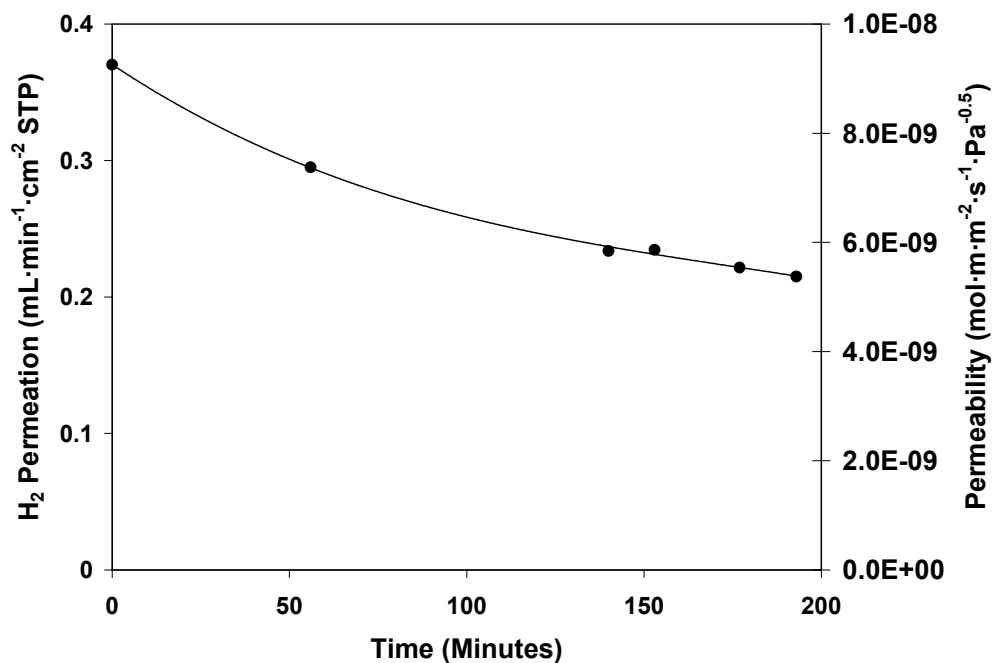


Figure 5. Degradation of hydrogen permeability over time at 750°C for a 0.83-mm thick cermet with 60 vol.% metal phase. There was no catalyst on the membrane. The feed gas was 80 mL/min 80/20 H₂/He and the sweep gas was 110 mL/min Ar.

A second set of membranes were prepared with only 40 vol.% metal phase, and the membranes were coated with a 0.1- μm thick Pd layer on each side. The results shown in Figure 6 demonstrate a maximum permeation rate of 0.18 mL/min/cm², which was roughly two times lower than the analog with 60 vol.% metal. This permeation rate corresponded to an apparent diffusivity of $3 \times 10^{-8} \text{ m}^2/\text{s}$, a permeability of $4 \times 10^{-9} \text{ mol m m}^{-2} \text{ s}^{-1} \text{ Pa}^{-0.5}$, and an E_a of 53 kJ/mol. Despite the Pd coating, post run X-ray diffraction analysis indicated formation of oxides of the metal phase on both sides of the membrane, and a hydride of the metal phase on the feed side. Subsequent SEM analysis revealed that the 0.1- μm Pd film was not sufficient to cover the membrane surface.

Although the cermet results were roughly two orders of magnitude lower than the metal composite, these data reflect only the first attempts at producing this category of membranes. These cermets were more than seven times thicker than the metal composite and only contained 40 to 60 vol.% metal. It is anticipated that hydrogen permeation will be improved by maximizing the metal content while reducing membrane thickness.

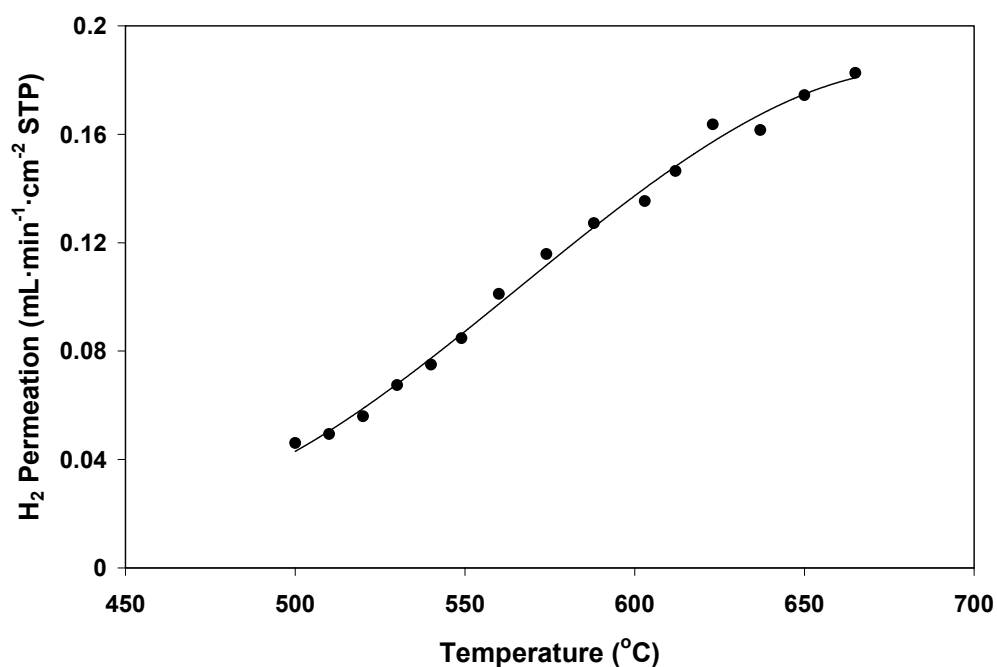


Figure 6. Hydrogen permeation as a function of temperature for a 0.75-mm thick cermet with 40 vol.% metal phase. The membrane contained a 0.1- μm thick Pd layer on each side. The feed gas was 80 mL/min 80/20 H₂/He and the sweep gas was 110 mL/min Ar.

CONCLUSIONS

Hydrogen separation membranes can be fabricated from proton conducting ceramics by incorporating a metal or electron conducting metal oxide phase. For the strictly ceramic membranes, there is good potential to achieve chemical stability by appropriate modification of the compositions. Unfortunately, these materials have low hydrogen permeation and extremely thin membranes would be necessary to achieve viable hydrogen separation rates. Hydrogen permeation through proton conducting cermet membranes was about an order of magnitude higher than the ceramics, and these materials had improved mechanical strength as well. These characteristics are much more

conducive to fabrication of thin film structures. When a metal with high hydrogen permeability was used in the cermets, the hydrogen separation rate increase approximately four-fold and the operation temperature range was broadened. Finally, inexpensive composite metal membranes achieved the highest hydrogen separation rates of all the membranes tested and the operating temperature range was more compatible with gas clean up technologies. Preliminary attempts to incorporate these hydrogen permeable metals into cermets were successful; however, the hydrogen separation rate was dramatically reduced and comparable to the proton conducting cermets.

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